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(19) (CA) **APPLICATION FOR CANADIAN PATENT** (12)

(54) Lithium Secondary Battery

(72) Nakane, Kenji - Japan ;  
Nishida, Yasunori - Japan ;  
Akamatsu, Chikashi - Japan ;  
Sato, Tomoari - Japan ;  
Tanino, Kazuyuki - Japan ;  
Yamamoto, Taketsugu - Japan ;

(71) SUMITOMO CHEMICAL COMPANY, LIMITED - Japan ;

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ABSTRACT OF THE DISCLOSURE

A lithium secondary battery includes a cathode containing, as an active material, a material that can be doped/undoped with lithium ions; an anode containing, as an active material, a lithium metal, a lithium alloy or a material that can be doped/undoped with lithium ions; and a liquid or solid electrolyte. In this lithium secondary battery, the active material used in the cathode is lithiated nickel dioxide containing gallium. As a result, the lithium secondary battery attains excellent cycle and overcharge resistance characteristics and has a high energy density.

## TITLE OF THE INVENTION

## LITHIUM SECONDARY BATTERY

## BACKGROUND OF THE INVENTION

## Field of the Invention

The present invention relates to a lithium secondary battery comprising a cathode including, as an active material, a material that can be doped/undoped with lithium ions, an anode including, as an active material, a lithium metal, a lithium alloy or a material that can be doped/undoped with lithium ions, and a liquid or solid electrolyte.

## Description of Related Art

Lithiated cobalt dioxide and lithiated nickel dioxide are compounds having a so-called  $\alpha$ - $\text{NaFeO}_2$  type structure in which lithium ions are regularly arranged in a layered manner alternately with cobalt ions or nickel ions vertically to a closest packing layer of oxygen ions. Due to this structure, the lithium ions in a layer can be diffused comparatively easily, and hence, lithium ions can be electrochemically doped or undoped in such a compound. Therefore, various study have been made so as to apply these compounds to a material for a cathode in a lithium secondary battery that is expected to play an important role as a high-performance

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compact secondary battery, and in the future, as a power supply for an electric vehicle or a power storage device for load leveling.

Lithiated cobalt dioxide is already practically used as a material for a cathode in a lithium secondary battery for supplying power to some of portable telephones and video cameras. In consideration of a material cost, however, lithiated cobalt dioxide, which is produced from an expensive cobalt compound, is inferior to lithiated nickel dioxide, which can be produced from an inexpensive and abundant nickel compound.

The charging/discharging characteristic of lithiated nickel dioxide, however, largely depends upon the synthesis method thereof, and therefore, it is regarded to be difficult to synthesize lithiated nickel dioxide having a large discharge capacity as compared with lithiated cobalt dioxide. The reason for the difficulty is considered as follows: In lithiated nickel dioxide, nickel is easily substituted at a lithium site, and therefore, the resultant compound includes nickel remained at the lithium site unless the synthesis condition is appropriately selected. The nickel remained at the lithium site inhibits the diffusion of lithium ions, thereby adversely affecting the charging/discharging charac-

teristic of the resultant lithiated nickel dioxide.

Recently, various attempts to synthesize lithiated nickel dioxide having a large discharge capacity have been made by optimizing the synthesis condition. For example, Yamada et al., (The 34th Battery Symposium, Lecture No. 2A06 (1993)) reported the following: lithiated nickel dioxide with an oxidation number of Ni of approximately 3.0 was obtained by firing a mixture of  $\text{LiOH} \cdot \text{H}_2\text{O}$  and  $\text{Ni}(\text{OH})_2$  in oxygen at a temperature of  $700^\circ\text{C}$ ; and when a mixture of the resultant lithiated nickel dioxide, acetylene black and polytetrafluoroethylene (hereinafter referred to as PTFE) was adhered with pressure to a current collector to manufacture a cathode, the discharge capacity was found to be 200 mAh/g through the evaluation by a constant capacity charge. They also reported that when the charge/discharge was continued to attain the discharge capacity of 200 mAh/g, the cycle characteristic was extremely poor and the lifetime was approximately merely ten cycles. It was reported that it was necessary to minimize the charge capacity for the constant capacity charge, i.e., the discharge capacity to be attained, in order to realize an excellent cycle characteristic, and that the charge capacity of 130 mAh/g or less led to a lifetime of 100 cycles or more.

Thus, lithiated nickel dioxide has a problem that the cycle characteristic is poor when it is charged/discharged at a high capacity.

On the other hand, lithiated nickel dioxide is inferior to lithiated cobalt dioxide in an energy density when used at the same capacity. This is because lithiated nickel dioxide has a lower discharging voltage. Generally, it is effective to increase the discharging voltage as well as the discharge capacity in order to obtain a secondary battery with a higher energy density. The discharging voltage, however, is defined as the characteristic of a material to be used, and hence, it has been impossible to increase the discharging voltage as far as pure lithiated nickel dioxide is used.

#### SUMMARY OF THE INVENTION

Considering the above-mentioned circumstance, the present inventors have made serious studies to find that a lithium secondary battery that can realize a high energy density and an excellent cycle characteristic even when charged/discharged at a high capacity by using lithiated nickel dioxide containing gallium as an active material in the cathode in a lithium secondary battery, which comprises the cathode including, as the active material, a material that can be doped/undoped with lithium ions, an anode includ-

ing, as an active material, a lithium metal, a lithium alloy or a material that can be doped/undoped with lithium ions and a liquid or solid electrolyte.

The lithium secondary battery of this invention comprises a cathode including, as an active material, a material that can be doped/undoped with lithium ions; an anode including, as an active material, a lithium metal, a lithium alloy or a material that can be doped/undoped with lithium ions; and a liquid or solid electrolyte. In this lithium secondary battery, the active material in the cathode is lithiated nickel dioxide containing gallium.

In a preferable embodiment, the lithiated nickel dioxide containing gallium satisfies the following relationship:

$$0 < x \leq 0.2$$

wherein  $x$  is a molar ratio of the gallium to a total amount of the gallium and nickel contained in the lithiated nickel dioxide.

In a more preferable embodiment, the lithiated nickel dioxide containing gallium satisfies the following relationship:

$$0 < x \leq 0.05$$

wherein  $x$  is a molar ratio of the gallium to a total amount of the gallium and nickel contained in the lithiated

nickel dioxide.

In a most preferable embodiment, the lithiated nickel dioxide containing gallium satisfies the following relationship:

$$0.001 < x \leq 0.02$$

wherein  $x$  is a molar ratio of the gallium to a total amount of the gallium and nickel contained in the lithiated nickel dioxide.

In one embodiment, the lithiated nickel dioxide containing gallium is obtained by firing a mixture of a lithium compound, a nickel compound, and gallium or a gallium compound.

In another embodiment, the lithiated nickel dioxide containing gallium is obtained by dispersing a nickel compound in an aqueous solution including a gallium compound and a water-soluble lithium salt, evaporating a water content of the resultant solution to obtain a mixture, and firing the mixture in an atmosphere containing oxygen.

In still another embodiment, the gallium compound is gallium nitrate, the water-soluble lithium salt is lithium nitrate and the nickel compound is basic nickel carbonate.

In still another embodiment, the lithiated nickel dioxide containing gallium is obtained by adding a basic



compound to an aqueous solution of gallium nitrate to attain pH of 10 or more, dissolving lithium nitrate in the resultant solution, adding basic nickel carbonate thereto, then evaporating a water content of the solution to obtain a mixture, and firing the mixture in an atmosphere containing oxygen.

In one embodiment, the basic compound is lithium hydroxide.

In one embodiment, the lithiated nickel dioxide containing gallium has a crystallite size of 700 angstrom or less determined through X-ray powder diffraction.

In one embodiment, the lithium secondary battery is charged at least once at 220 mAh/g or more per weight, at the time of the production thereof, of the lithiated nickel dioxide containing gallium.

In one embodiment, the anode includes graphite as a sole component or main component of an active material, and the liquid electrolyte comprises ethylene carbonate, dimethyl carbonate and ethyl methyl carbonate.

The objective of the present invention is providing a lithium secondary battery having a high energy density and exhibiting excellent cycle and overcharge resistance characteristics even when charged/discharged at a high capacity.

**BRIEF DESCRIPTION OF THE DRAWINGS**

Figure 1 is a graph showing the variation with cycles of the discharge capacity of lithium secondary batteries of an example and comparative examples;

Figure 2 is a graph showing the variation with cycles of the average discharging voltages of the lithium secondary batteries of the example and the comparative examples;

Figure 3 is a graph showing the discharging curves of the lithium secondary batteries of the example and the comparative example;

Figure 4 is a graph showing the variation with cycles of the discharge capacities of lithium secondary batteries of other examples and another comparative example;

Figure 5 shows the results of powder X-ray diffraction performed on the cathode active materials of the examples;

Figure 6 is a graph showing the variation with cycles of the discharge capacities of lithium secondary batteries of still other examples and another comparative example; and

Figure 7 is a graph showing the variation with cycles of the discharge capacities of lithium secondary batteries of examples.

**DESCRIPTION OF THE PREFERRED EMBODIMENTS**

The present invention will now be described in detail.

A cathode of a lithium secondary battery of this invention includes, as an active material, a material that can be doped/undoped with lithium ions, and the material that can be doped/undoped with lithium ions is herein lithiated nickel dioxide containing gallium.

As a method for adding gallium to lithiated nickel dioxide, previously synthesized lithiated nickel dioxide can be mixed with gallium or a gallium compound to be fired. However, in order to simplify the production process and homogeneously add a small amount of gallium, it is preferred that a lithium compound, a nickel compound, and gallium or a gallium compound are mixed with one another to be fired. Alternatively, a nickel compound and gallium or a gallium compound can be first mixed with each other to be fired, and then the fired mixture can be mixed with a lithium compound to be fired again. Similarly, a lithium compound and gallium or a gallium compound can be first mixed with each other to be fired, and then the fired mixture can be mixed with a nickel compound to be fired again.

Examples of the lithium compound used in the invention includes lithium carbonate, lithium nitrate and lithium hydroxide. Examples of the nickel compound used in the invention includes nickel oxide, nickel hydroxide, nickel

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nitrate, nickel carbonate  $\text{NiCO}_3 \cdot w\text{H}_2\text{O}$  (wherein  $w \geq 0$ ), basic nickel carbonate  $x\text{NiCO}_3 \cdot y\text{Ni}(\text{OH})_2 \cdot z\text{H}_2\text{O}$  (wherein  $x > 0$ ,  $y > 0$  and  $z > 0$ ) and acidic nickel carbonate  $\text{Ni}_m\text{H}_2\text{n}(\text{CO}_3)_{m+n}$  (wherein  $m > 0$  and  $n > 0$ ). As a raw material for gallium to be added, a gallium compound such as metal gallium, gallium oxide, gallium nitrate and gallium hydroxide can be used. In particular, a preferred gallium compound is a water-soluble gallium salt such as gallium nitrate.

The following is a preferred method for mixing the lithium compound, the nickel compound and the gallium compound and firing the obtained mixture: The nickel compound is dispersed in an aqueous solution including the gallium compound and the water-soluble lithium salt, and the water content of the obtained solution is evaporated. The thus obtained mixture is fired in an atmosphere containing oxygen. In this method, the water-soluble lithium salt can be homogeneously mixed with the gallium compound and the nickel compound. Therefore, the resultant lithiated nickel dioxide is free from lacking lithium in some portions due to ununiformity of the mixed components.

As a result of further study, the present inventors found a preferred combination of the materials as follows: gallium nitrate is preferably used as the gallium compound,

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lithium nitrate as the water-soluble lithium salt, and basic nickel carbonate as the nickel compound. When the lithiated nickel dioxide containing gallium obtained from these materials is used in a cathode, the resultant lithium secondary battery is found to realize a high energy density.

When gallium nitrate, lithium nitrate and basic nickel carbonate are used as the gallium compound, the water-soluble lithium salt and the nickel compound, respectively, an aqueous solution of gallium nitrate and lithium nitrate is acidic. When basic nickel carbonate is added to this aqueous solution, carbon dioxide is generated and gallium hydroxide is precipitated therein. Therefore, gallium is actually added to and mixed in the solution as gallium hydroxide.

As a result of further study to improve the above-mentioned method, the present inventors found the following: When the pH of an aqueous solution of gallium nitrate is increased to exceed 10, the solution once becomes cloudy due to the precipitation of gallium hydroxide, and then suddenly becomes less cloudy, and becomes substantially transparent at pH of 11 or more. When the solution has pH of 10 or more, gallium is regarded to be dispersed in the solution as gallium hydroxide in the shape of extremely fine colloid, or to be dissolved in the solution as dioxogallate

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ions  $\text{GaO}_2^-$ . Accordingly, after a basic compound is added to the aqueous solution of gallium nitrate to increase pH of the solution to exceed 10, lithium nitrate is then dissolved in the solution, and basic nickel carbonate is also dispersed in the solution. The water content of the thus obtained solution is evaporated, and the resultant mixture is fired in an atmosphere containing oxygen. When this method is adopted, gallium can be homogeneously mixed with the other materials because, as described above, it is dispersed as gallium hydroxide in the shape of extremely fine colloid or dissolved as dioxogallate ions  $\text{GaO}_2^-$ . In this method, side production of a composite oxide of lithium and gallium, which makes no contribution to charge/discharge, can be suppressed, and hence, this method is particularly preferred when only a small amount of gallium is to be added.

Further, when lithium hydroxide, lithium oxide or lithium peroxide is used as the basic compound to increase the pH of the gallium nitrate solution, lithium nitrate is remained as a result of the neutralization reaction between such a lithium compound and the solution. Lithium nitrate, however, is consumed in and has no harmful effect on the production of lithiated nickel dioxide containing gallium. Therefore, the above-mentioned basic compounds are preferred,

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among which lithium hydroxide is most preferable because of its inexpensiveness and easiness in handling.

The above-mentioned mixture is fired preferably in an atmosphere containing oxygen, more preferably in oxygen, and most preferably in an oxygen stream.

The firing temperature is preferably in the range between 350°C and 800°C, and more preferably in the range between 600°C and 750°C. When the firing temperature exceeds 800°C, the resultant lithiated nickel dioxide includes a larger ratio of a rock salt domain in which lithium ions and nickel ions are irregularly arranged, which results in inhibition of reversible charge/discharge. When the firing temperature is below 350°C, the generation reaction for lithiated nickel dioxide is scarcely effected.

The firing time is preferably 2 hours or more, and more preferably 5 hours or more.

The amount of gallium to be added is preferably as small as possible since gallium or a gallium compound is expensive. Specifically, when a molar ratio of gallium to be mixed to the total amount of the gallium and the nickel compound is taken as  $x$ , the relationship of  $0 < x \leq 0.2$  is preferably satisfied. When  $x$  is less than 0.05, the diffraction peak in X-ray powder diffraction of a composite oxide of

lithium and gallium, which makes no contribution to the reversible charge/discharge, has a smaller intensity, or there appears no diffraction peak of the composite oxide of lithium and gallium. This is advantageous in consideration of the discharge capacity per volume or weight. Therefore, the relationship of  $0 < x \leq 0.05$  is more preferably satisfied. Further, taking both the discharge capacity and the cycle characteristic into consideration, the relationship of  $0.001 < x \leq 0.02$  is most preferably satisfied.

Furthermore, the present inventors examined the relationship between the cycle characteristic and a crystallite size obtained through the X-ray powder diffraction of lithiated nickel dioxide containing gallium. As a result, the inventors found that lithiated nickel dioxide with a crystallite size of 700 angstrom or less exhibits an excellent cycle characteristic and overcharge resistance. Thus, the present invention was accomplished.

The cathode of the lithium secondary battery of the present invention includes, as an active material, the above-mentioned lithiated nickel dioxide containing gallium, and can further include, as additional components, a carbonaceous material as a conductive substance and a thermoplastic resin as a binder.



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Examples of the carbonaceous material include natural graphite, artificial graphite and cokes. Examples of the thermoplastic resin include poly(vinylidene fluoride) (hereinafter referred to as PVDF), PTFE, polyethylene and polypropylene.

The anode of the present lithium secondary battery includes a lithium metal, a lithium alloy or a material that can be doped/undoped with lithium ions. Examples of the material that can be doped/undoped with lithium ions include carbonaceous materials such as natural graphite, artificial graphite, cokes, carbon black, pyrolytic carbons, carbon fibers and fired products of organic polymer compounds. Among the carbonaceous materials, the graphitic materials such as a natural graphite or an artificial graphite are more preferable than others for anode, because of the flatness of their charging/discharging potential and of their low average working potential which, when combined with a cathode, provide high energy density. The carbonaceous material can be in any shape including a flake, a sphere, a fiber or an agglomerate of fine powder. The anode can further include a thermoplastic resin as a binder, if necessary. Examples of the thermoplastic resin include PVDF, PTFE, polyethylene and polypropylene.

The electrolyte of the present lithium secondary battery can be liquid or solid. An example of the liquid electrolyte includes a nonaqueous liquid electrolyte in which a lithium salt is dissolved in an organic solvent. An example of the solid electrolyte includes a so-called solid electrolyte.

The lithium salt to be dissolved in the nonaqueous liquid electrolyte is one of or a combination of two or more of  $\text{LiClO}_4$ ,  $\text{LiPF}_6$ ,  $\text{LiAsF}_6$ ,  $\text{LiSbF}_6$ ,  $\text{LiBF}_4$ ,  $\text{LiCF}_3\text{SO}_3$ ,  $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ ,  $\text{Li}_2\text{B}_{10}\text{Cl}_{10}$ , lower aliphatic lithium carboxylate and  $\text{LiAlCl}_4$ .

Examples of the organic solvent include carbonates such as propylene carbonate, ethylene carbonate, dimethyl carbonate, diethyl carbonate and ethyl methyl carbonate; ethers such as 1,2-dimethoxyethane, 1,3-dimethoxypropane, tetrahydrofuran and 2-methyltetrahydrofuran; esters such as methyl formate, methyl acetate and  $\gamma$ -butyrolactone; nitriles such as acetonitrile and butyronitrile; amides such as N,N-dimethylformamide, and N,N-dimethylacetamide; carbamates such as 3-methyl-2-oxazolidone; and sulfur-containing compounds such as sulfolane, dimethylsulfoxide and 1,3-propanesultone. Generally, a combination of two or more of these compounds is used. In particular, a mixed solvent including a carbonate is preferably used, and a mixed solvent of a

combination of a cyclic carbonate and a noncyclic carbonate or a combination of a cyclic carbonate and an ether is more preferably used. Among the mixed solvents of cyclic carbonates and non-cyclic carbonates, the solvents which comprise ethylene carbonate, dimethyl carbonate, and ethyl methyl carbonate are more preferable than others, because they provide wide operating temperature range and excellent drain capability and they are hardly decomposed when they are used with the anode including said graphitic materials.

Examples of the solid electrolyte includes polymer electrolyte such as polyethylene oxide polymer compounds and polymer compounds including at least one of a polyorganosiloxane branch and a polyoxyalkylene branch; sulfide type electrolyte such as  $\text{Li}_2\text{S-SiS}_2$ ,  $\text{Li}_2\text{S-GeS}_2$ ,  $\text{Li}_2\text{S-P}_2\text{S}_5$ , and  $\text{Li}_2\text{S-B}_2\text{S}_3$ , and inorganic compound type electrolyte including sulfide such as  $\text{Li}_2\text{S-SiS}_2\text{-Li}_3\text{PO}_4$  and  $\text{Li}_2\text{S-SiS}_2\text{-Li}_2\text{SO}_4$ . Further, a so-called gel type electrolyte in which a nonaqueous liquid electrolyte is held by a polymer can be used.

The shape of the present lithium secondary battery is not particularly specified, and can be in any shape including paper, a coin, a cylinder and a rectangular parallelepiped.

According to the present invention, the lithium secondary battery can attain an excellent cycle characteristic even

when charged/discharged at a high capacity, and also can attain a high energy density because it has a higher discharging voltage than a conventional lithium secondary battery using pure lithiated nickel dioxide. Although it is not very clear why the present lithium secondary battery attains these excellent characteristics, the following is considered to be the reason: the structure of lithiated nickel dioxide is stabilized when charged/discharged, especially when deeply charged, by incorporation of gallium into the crystal structure of lithiated nickel dioxide in some way, or by suppressing the growth of the crystallite of lithiated nickel dioxide by gallium.

In a battery using pure lithiated nickel dioxide, when it is charged by using lithium as a counter electrode, an open circuit voltage (hereinafter referred to as OCV) increases as the charge capacity increases. It is observed that when the charge capacity exceeds approximately 200 mAh/g, the OCV no longer increases but remains constant at 4.18 V, a potential against lithium. Whereas in the battery using lithiated nickel dioxide containing gallium, the OCV does not remain constant at 4.18 V but further increases as the charge capacity increases. Further, the charging/discharging curve of the battery using pure lithiated

nickel dioxide has several inflection points that can be regarded to correspond to the change of its crystal structure, while the charging/discharging curve of the battery using lithiated nickel dioxide containing gallium is smooth and it is difficult to identify such an inflection point in this curve. From these facts, it is considered that the gallium added to the lithiated nickel dioxide affects the crystal structure or the crystallite size of the lithiated nickel dioxide in some way.

The present lithium secondary battery using lithiated nickel dioxide containing gallium as an active material for the cathode exhibits a high energy density and has an excellent cycle characteristic even when charged/discharged at a high capacity. The lithium secondary battery, however, exhibited a comparatively large overvoltage at an initial stage, the reason for which is not apparent. Therefore, at first, the battery had a problem that several charging/discharging cycles were required to settle the overvoltage, namely, the rise of the discharge capacity of the battery was delayed.

The present inventors made further study to overcome this problem, and found that a quick rise of the discharge capacity can be attained by decreasing the overvoltage at the

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initial stage through conducting at least one charge at 220 mAh/g per weight of lithiated nickel dioxide containing gallium at the time of the production thereof.

[Examples]

The present invention will now be described in more detail by way of examples, which do not limit the invention. An electrode and a plate battery for a charging/discharging test were manufactured as follows, unless otherwise mentioned:

To a mixture of lithiated nickel dioxide or lithiated nickel dioxide containing gallium, that is, an active material, and acetylene black as a conductive substance was added a 1-methyl-2-pyrrolidone (hereinafter referred to as NMP) solution including PVDF as a binder so as to attain a composition ratio among the active material, the conductive substance and the binder of 91:6:3 (weight ratio). The resultant solution was kneaded to obtain a paste. The paste was coated over a #200 stainless mesh, which was to work as a current collector, and the mesh bearing the paste was dried in vacuum at a temperature of 150°C for 8 hours. Thus, an electrode was produced.

By using the thus obtained electrode, a plate battery was manufactured together with a liquid electrolyte described

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below, a polypropylene microporous membrane as a separator and metal lithium as a counter electrode (i.e., an anode). The used liquid electrolyte was a solution in which  $\text{LiClO}_4$  was dissolved at a proportion of 1 molar/litter in a 1:1 mixture of propylene carbonate (hereinafter referred to as PC) and 1,2-dimethoxyethane (hereinafter referred to as DME) (Hereinafter this liquid electrolyte is referred to as  $\text{LiClO}_4/\text{PC}+\text{DME}$ .); or a solution in which  $\text{LiPF}_6$  was dissolved at a proportion of 1 molar/litter in a 30:35:35 mixture of ethylene carbonate (hereinafter referred to as EC), dimethyl carbonate (hereinafter referred to as DMC) and ethyl methyl carbonate (hereinafter referred to as EMC) (Hereinafter this liquid electrolyte is referred to as  $\text{LiPF}_6/\text{EC}+\text{DMC}+\text{EMC}$ .).

The X-ray powder diffraction was conducted by using a RAD-IIC system (manufactured by Rigaku Corporation) under the following condition:

X-ray:  $\text{CuK}\alpha$  (monochromatized by a graphite curved monochromator)

Voltage - current: 40 kV - 30 mA

Range of measured angle:  $2\theta = 15$  to  $140^\circ$

Slit: DS- $1^\circ$ , RS-0.15 mm, SS- $1^\circ$

Step:  $0.02^\circ$

Counting time: 1 second

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Obtained data were processed by using an MXP system (manufactured by Mac Science Co., Ltd.) as follows: First, a true profile was obtained by a Stokes method, and then a crystallite size was calculated by a Warren & Averbach method.

Example 1:

First, 2.09 g of gallium nitrate ( $\text{Ga}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ; manufactured by Kojundo Chemical Laboratory Co., Ltd.; 3N graded reagent), 7.23 g of lithium nitrate (manufactured by Wako Pure Chemical Industries, Ltd.; guaranteed graded reagent) were dissolved in 15.1 g of water. Then, 11.91 g of basic nickel carbonate ( $\text{NiCO}_3 \cdot 2\text{Ni}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ ; manufactured by Wako Pure Chemical Industries, Ltd.; graded reagent) was added to and homogeneously dispersed in the obtained solution. The water content of the resultant solution was evaporated, and the obtained mixture was charged in a tubular furnace having an alumina core tube to be fired in an oxygen stream of 50  $\text{cm}^3/\text{min.}$  at a temperature of  $660^\circ\text{C}$  for 15 hours. At this point, a molar ratio  $x$  of gallium to the total amount of gallium and nickel was set to be 0.05.

By using the thus obtained powder, a plate battery (in which a liquid electrolyte was  $\text{LiClO}_4/\text{PC}+\text{DME}$ ) was manufactured to be subjected to a charging/discharging test under



the condition of a maximum charging voltage of 4.3 V, a minimum discharging voltage of 2.5 V and a constant current of 0.17 mA/cm<sup>2</sup>. During the charging/discharging test, a resting time of 2 hours was provided between the termination of the charge and the start of the discharge so as to settle an overvoltage, and the voltage immediately before the start of the discharge was regarded as the OCV after the termination of the charge. The OCVs after the termination of the charge in the 5th cycle and the 20th cycle were both 4.22 V.

Figure 1 shows the variation of the discharge capacity up to the 30th cycle. The discharge capacity in the 30th cycle was 171 mAh/g, and thus the battery exhibited an excellent cycle characteristic.

Figure 2 shows the variation of the average discharging voltage up to the 30th cycle. The average discharging voltage in the 30th cycle was kept at 3.80 V.

Figure 3 shows the discharging curve in the first cycle. In this graph, the discharge capacity is normalized for comparison. This graph reveals that the discharging curve obtained by using lithiated nickel dioxide containing gallium is smooth and that it is difficult to identify an inflection point that is conventionally observed in using pure lithiated nickel dioxide.

## Comparative Example 1:

First, 94.1 g of lithium nitrate (manufactured by Wako Pure Chemical Industries, Ltd.; guaranteed graded reagent) was dissolved in 150 g of water, and then 163.0 g of basic nickel carbonate ( $\text{NiCO}_3 \cdot 2\text{Ni}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ ; manufactured by Wako Pure Chemical Industries, Ltd.; graded reagent) was added thereto to be homogeneously dispersed. The water content of the resultant solution was evaporated, and the obtained mixture was charged in a tubular furnace having an alumina core tube to be fired in an oxygen stream of  $50 \text{ cm}^3/\text{min}$ . at a temperature of  $720^\circ\text{C}$  for 5 hours.

By using the thus obtained powder, a plate battery (in which a liquid electrolyte was  $\text{LiClO}_4/\text{PC}+\text{DME}$ ) was manufactured to be subjected to a charging/discharging test under the condition of a maximum charging voltage of 4.9 V, a minimum discharging voltage of 2.5 V and a constant current of  $0.17 \text{ mA}/\text{cm}^2$ . During the charging/discharging test, a resting time of 2 hours was provided between the termination of the charge and the start of the discharge so as to settle an overvoltage, and the voltage immediately before the start of the discharge was regarded as the OCV after the termination of the charge. The OCVs after the termination of the charge in the 5th cycle and the 20th cycle were both 4.18 V.

The variation of the discharge capacity up to the 30th cycle is shown in Figure 1. The discharge capacity in the 30th cycle was 161 mAh/g, which was largely degraded as compared with the discharge capacity in the initial stage of the test.

The variation of the average discharging voltage up to the 30th cycle is shown in Figure 2. The average discharging voltage in the 30th cycle was 3.70 V, which was lower by 0.1 V than that of the battery of Example 1. The discharging curve in the first cycle is shown in Figure 3. In this graph, the discharge capacity is normalized for comparison. The discharge capacity of this battery has a complicated shape having several inflection points that are regarded to correspond to the change of the crystal structure. This discharging curve is apparently different from that of the battery using lithiated nickel dioxide containing gallium.

Comparative Example 2:

By using the powder of lithiated nickel dioxide obtained in Comparative Example 1, a plate battery (in which a liquid electrolyte was  $\text{LiClO}_4/\text{PC}+\text{DME}$ ) was similarly manufactured to be subjected to a charging/discharging test under the condition of a maximum charging voltage of 4.2 V, a minimum discharging voltage of 2.5 V and a constant current

of 0.17 mA/cm<sup>2</sup>.

The variation of the discharge capacity and that of the average discharging voltage up to the 10th cycle are shown in Figures 1 and 2, respectively. The discharge capacity in the 10th cycle was 169 mAh/g. Thus, when the maximum charging voltage is decreased, the cycle characteristic is improved, whereas the discharge capacity is decreased. The average discharging voltage in the 10th cycle was 3.73 V, which was lower by approximately 0.1 V than that of the battery of Example 1.

Example 2:

First, 0.235 g of gallium oxide (manufactured by Kojundo Chemical Laboratory Co., Ltd.; 3N graded reagent), 3.62 g of lithium nitrate (manufactured by Wako Pure Chemical Industries, Ltd.; guaranteed graded reagent), and 5.96 g of basic nickel carbonate ( $\text{NiCO}_3 \cdot 2\text{Ni}(\text{OH}) \cdot 4\text{H}_2\text{O}$ ; manufactured by Wako Pure Chemical Industries, Ltd.; graded reagent) were homogeneously mixed in an agate mortar. The obtained mixture was charged in a tubular furnace having an alumina core tube to be fired in an oxygen stream of 50 cm<sup>3</sup>/min. at a temperature of 660°C for 15 hours. At this point, a molar ratio  $x$  of gallium to the total amount of gallium and nickel was set to be 0.05.

By using the thus obtained powder, a plate battery (in which an liquid electrolyte was  $\text{LiClO}_4/\text{PC}+\text{DME}$ ) was manufactured to be subjected to a charging/discharging test under the condition of a maximum charging voltage of 4.3 V, a minimum discharging voltage of 2.5 V, and a constant current of  $0.17 \text{ mA/cm}^2$ . During the charging/discharging test, a resting time of 2 hours was provided between the termination of the charge and the start of the discharge so as to settle an overvoltage, and the voltage immediately before the start of the discharge was regarded as the OCV after the termination of the charge. The OCVs after the termination of the charge in the 5th cycle and the 20th cycle were both 4.22 V.

The discharge capacity in the 30th cycle was 165 mAh/g and the average discharging voltage in the 30th cycle was 3.78 V.

Comparative Example 3:

By using the powder obtained in Comparative Example 1, a plate battery (in which a liquid electrolyte was  $\text{LiClO}_4/\text{PC}+\text{DME}$ ) was manufactured to be subjected to a charging/discharging test using charge by a constant current and voltage and discharge by a constant current under the following condition:

Maximum charging voltage: 4.3 V

Charging time: 6 hours

Charging current: 1 mA/cm<sup>2</sup>

Minimum discharging voltage: 2.5 V

Discharging current: 0.17 mA/cm<sup>2</sup>

Above-mentioned charge by a constant current and voltage will be described in more detail. At first a battery is charged up to a maximum charging voltage (4.3 V in this Comparative Example) with a constant charging current (1 mA/cm<sup>2</sup> in this Comparative Example), then the charging current is decreased to keep the voltage of the battery as high as the maximum charging voltage. The charge is terminated when total charging time reaches a predetermined charging time (6 hours in this Comparative Example).

The discharge capacity up to the 20th cycle is shown in Figure 4. As compared with the battery of Comparative Example 1, this battery was degraded with cycles faster because it was charged with a constant current and voltage under a severer condition, namely, it was supplied with a voltage of 4.3 V for a longer time, although it was discharged in the same manner as in Comparative Example 1.

Example 3:

By using the powder obtained in Example 1, a plate battery (in which a liquid electrolyte was LiClO<sub>4</sub>/PC+DME) was

manufactured to be subjected to a charging/discharging test using charge by a constant current and voltage and discharge by a constant current under the same condition as in Comparative Example 3.

The variation of the discharge capacity up to the 20th cycle is shown in Figure 4. Although the capacity is slightly decreased with that in the 10th cycle as a peak, this battery exhibited a superior cycle characteristic as compared with the battery containing no gallium (i.e., Comparative Example 3) even when the battery was charged more severely with a constant current and voltage.

Example 4:

First, 108.6 g of lithium nitrate (manufactured by Wako Pure Chemical Industries, Ltd.; guaranteed graded reagent) was dissolved in 150 g of water. Then, to the resultant solution were added 9.06g of gallium hydroxide ( $\text{Ga}(\text{OH})_3$ ; manufactured by Kojundo Chemical Laboratory Co., Ltd.; 3N graded reagent) and 190.5 g of basic nickel carbonate ( $\text{NiCO}_3 \cdot 2\text{Ni}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ ; manufactured by Wako Pure Chemical Industries, Ltd.; graded reagent) to be homogeneously dispersed. The water content of the resultant solution was evaporated. The obtained mixture was charged in a tubular furnace having an alumina core tube to be fired in an oxygen

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stream of 50 cm<sup>3</sup>/min. at a temperature of 660°C for 15 hours. At this point, a molar ratio  $x$  of gallium to the total amount of gallium and nickel was set to be 0.05.

By using the thus obtained powder, a plate battery (in which a liquid electrolyte was LiClO<sub>4</sub>/PC+DME) was manufactured to be subjected to a charging/discharging test using charge by a constant current and voltage and discharge by a constant current under the same condition as in Example 3.

The variation of the discharge capacity up to the 20th cycle is shown in Figure 4. Although the discharge capacity in the initial stage was small and the rise of the discharge capacity was delayed, the battery exhibited an excellent cycle characteristic from the 8th cycle on, even when charged with the constant current and voltage.

The X-ray diffraction of the obtained powder is shown in Figure 5. In this powder, a small amount of a composite oxide of lithium and gallium, LiGaO<sub>2</sub>, was found.

Example 5:

First, 13.64 g of gallium nitrate (Ga(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O; manufactured by Kojundo Chemical Laboratory Co., Ltd.; 3N graded reagent) and 12.06 g of lithium nitrate (manufactured by Wako Pure Chemical Industries, Ltd.; guaranteed graded reagent) were dissolved in 19.3 g of water. Then, 16.72 g of basic



nickel carbonate ( $\text{NiCO}_3 \cdot 2\text{Ni}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ ; manufactured by Wako Pure Chemical Industries, Ltd.; graded reagent) was added to and homogeneously dispersed in the obtained solution, and the water content of the resultant solution was evaporated. The obtained mixture was charged in a tubular furnace having an alumina core tube to be fired in an oxygen stream of 50  $\text{cm}^3/\text{min.}$  at a temperature of  $660^\circ\text{C}$  for 15 hours. At this point, a molar ratio  $x$  of gallium to the total amount of gallium and nickel was set to be 0.2.

By using the thus obtained powder, a plate battery (in which a liquid electrolyte was  $\text{LiClO}_4/\text{PC}+\text{DME}$ ) was manufactured to be subjected to a charging/discharging test using charge by a constant current and voltage and discharge by a constant current under the same condition as in Example 3.

The variation of the discharge capacity up to 20th cycle is shown in Figure 4. Although the discharge capacity was as small as 120  $\text{mAh/g.}$ , the battery exhibited an excellent cycle characteristic even when charged with a constant current and voltage.

The result of the X-ray diffraction of the obtained powder is shown in Figure 5. In this powder, a large amount of the composite oxide of lithium and gallium,  $\text{LiGaO}_2$ , was found. The cycle characteristic was improved by the addition

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of gallium in this battery, but it had a disadvantageously small discharge capacity per weight due to the presence of a large amount of the compound making no contribution to the charge/discharge. It is regarded that the compound blocks a conductive path in the battery, thereby making the discharge capacity small.

Example 6:

First, 6.97 g of gallium nitrate ( $\text{Ga}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ; manufactured by Kojundo Chemical Laboratory Co., Ltd.; 3N graded reagent) was dissolved in 33.5 g of water. The pH of the obtained solution was 1.47. Then, 2.61 g of lithium hydroxide monohydrate ( $\text{LiOH} \cdot \text{H}_2\text{O}$ ; manufactured by Wako Pure Chemical Industries, Ltd.; guaranteed graded reagent) was added to and dissolved in the solution. The resultant solution became cloudy once and then became transparent. The pH of the solution at this point was 11.16. Then, 20.67 g of lithium nitrate (manufactured by Wako Pure Chemical Industries, Ltd.; guaranteed graded reagent) was dissolved in the solution, and 42.34 g of basic nickel carbonate ( $\text{NiCO}_3 \cdot 2\text{Ni}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ ; manufactured by Wako Pure Chemical Industries, Ltd.; graded reagent) was successively added thereto to be homogeneously dispersed. The water content of the resultant solution was evaporated, and the thus obtained mixture was charged in a

tubular furnace having an alumina core tube to be fired in an oxygen stream of 50 cm<sup>3</sup>/min. at a temperature of 660°C for 15 hours. A molar ratio  $x$  of gallium to the total amount of gallium and nickel was set to be 0.05.

By using the thus obtained powder, a plate battery (in which a liquid electrolyte was LiClO<sub>4</sub>/PC+DME) was manufactured to be subjected to a charging/discharging test using charge by a constant current and voltage and discharge by a constant current under the same condition as in Example 3.

The variation of the discharge capacity up to 20th cycle is shown in Figure 4. This battery had a quicker rise of the discharge capacity than that of Example 4, and exhibited a superior cycle characteristic to that of Example 3 from the 7th cycle on.

The result of the x-ray diffraction of the obtained powder is shown in Figure 5. In this powder, no diffraction line of the composite oxide of lithium and gallium, LiGaO<sub>2</sub>, was found.

#### Comparative Example 4:

By using the powder obtained in Comparative Example 1, a plate battery (in which a liquid electrolyte was LiPF<sub>6</sub>/EC+DMC+EMC) was manufactured to be subjected to a charging/discharging test using charge by a constant current

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and voltage and discharge by a constant current under the following condition:

Maximum charging voltage: 4.3 V

Charging time: 8 hours

Charging current: 0.3 mA/cm<sup>2</sup>

Minimum discharging voltage: 3.0 V

Discharging current: 0.3 mA/cm<sup>2</sup>

The variation of the discharge capacity up to 20th cycle is shown in Figure 6. Further, a capacity holding ratio R1 from the 1st cycle to the 10th cycle (i.e., the discharge capacity in the 10th cycle/the discharge capacity in the 1st cycle) and a capacity holding ratio R2 from the 11th cycle to the 20th cycle (i.e., the discharge capacity in the 20th cycle/the discharge capacity in the 11th cycle) are listed in Table 1 below. Although the battery was degraded less and less through the cycles, the discharge capacity was largely decreased as compared with that at the initial stage.

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Table 1:

	X	R1	R2	Crystallite size (Å)
Comparative 4	0	0.783	0.862	810
Example 7	0.05	1.239	1.023	320
	0.02	1.124	1.005	330
	0.01	1.048	0.979	370
	0.005	1.047	0.969	360
	0.001	1.058	0.949	430

## Example 7:

Gallium nitrate ( $\text{Ga}(\text{NO}_3)_3 \cdot 6.2\text{H}_2\text{O}$ ; manufactured by Kojundo Chemical Laboratory Co., Ltd. ; 3N graded reagent), lithium nitrate (manufactured by Wako Pure Chemical Industries, Ltd.; guaranteed graded reagent) and basic nickel carbonate ( $\text{NiCO}_3 \cdot 2\text{Ni}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ ; manufactured by Wako Pure Chemical Industries, Ltd.; graded reagent) were weighed so as to achieve molar ratios  $x$  of gallium to the total amount of gallium and nickel of 0.05, 0.02, 0.01, 0.005 and 0.001, and the thus weighed compounds were mixed to obtain five kinds of mixtures as follows: Each of the desired amounts of gallium nitrate was dissolved in water, and lithium hydroxide monohydrate ( $\text{LiOH} \cdot \text{H}_2\text{O}$ ; manufactured by Wako Pure chemical Industries, Ltd.; guaranteed graded reagent) was added thereto to adjust the pH of the resultant solution. The pH was adjusted to be 11.1, 11.2, 11.4, 11.2 and 10.6 in the solutions having the molar ratios  $x$  of 0.05, 0.02, 0.01, 0.005 and 0.001, respectively. Then, basic nickel carbonate was added to the respective solutions to be homogeneously dispersed, and the water contents of the solutions were evaporated. Each of the resultant mixtures was charged in a tubular furnace having an alumina core tube to be fired in an oxygen stream of 50  $\text{cm}^3/\text{min.}$  at a temperature of  $660^\circ\text{C}$  for 15 hours. At this

point, a molar ratio of lithium to the total amount of gallium and nickel was set to be 1.05 in each solution.

By using the thus obtained powder, plate batteries (in which a liquid electrolyte was  $\text{LiPF}_6/\text{EC}+\text{DMC}+\text{EMC}$ ) were manufactured to be subjected to a charging/discharging test using charge by a constant current and voltage and discharge by a constant current under the same condition as in Comparative Example 4.

The variation of the discharge capacity of each battery up to the 20th cycle is shown in Figure 6. Further, a capacity holding ratio R1 from the 1st cycle to the 10th cycle (i.e., the discharge capacity in the 10th cycle/the discharge capacity in the 1st cycle) and a capacity holding ratio R2 from the 11th cycle to the 20th cycle (i.e., the discharge capacity in the 20th cycle/the discharge capacity in the 11th cycle) are listed in Table 1 above.

The results shown in Figure 6 and Table 1 reveal that the batteries exhibited an excellent cycle characteristic as compared with a battery containing no gallium, regardless of the molar ratio  $x$ . Further, in all the batteries, the discharge capacity was rather small at the initial stage of the test and was increased as the test proceeded, also regardless of the molar ratio  $x$ . The reason for this phenomenon is not

very clear, but the phenomenon is found to correspond to the process of a comparatively large overvoltage at the initial stage being gradually settled. The quickness of the settlement of the overvoltage, the discharge capacity attained when the increase of the capacity is stabilized, and the cycle characteristic attained thereafter depend upon the molar ratio  $x$ . Specifically, as the molar ratio  $x$  decreases from 0.05, the settlement of the overvoltage becomes faster (i.e., it is settled by approximately the 5th cycle), and the discharge capacity attained when the increase of the capacity is stabilized becomes larger. With regard to the cycle characteristic, the capacity is not decreased at all when  $0.02 \leq x \leq 0.05$ , while it is slightly decreased when  $x < 0.02$ . Accordingly, a preferable range of the molar ratio  $x$  is  $0.001 < x \leq 0.02$ , taking both the discharge capacity and the cycle characteristic into consideration.

Comparative Example 5:

The powder obtained in Comparative Example 1 was subjected to the X-ray powder diffraction, thereby obtaining a crystallite size in accordance with the above-mentioned method. The obtained result is listed in Table 1. By using this powder, a plate battery (in which a liquid electrolyte was  $\text{LiPF}_6/\text{EC}+\text{DMC}+\text{EMC}$ ) was manufactured to be subjected to an



overcharging test in the following manner:

The battery was charged by a constant current and voltage under a condition of a maximum charging voltage of 4.2 V, a charging current of 0.3 mA/cm<sup>2</sup> and a charging time of 40 hours. Then, the battery was discharged by a constant current under a condition of a minimum discharging voltage of 3.0 V and a discharging current of 0.3 mA/cm<sup>2</sup>. At this point, the charge capacity was 263 mAh/g and the discharge capacity was 221 mAh/g. When the charge/discharge was repeated under the same condition, the charge capacity and the discharge capacity became 219 mAh/g and 214 mAh/g, respectively. In this manner, the battery using this powder was excessively charged, resulting in degrading the efficiency of the charge/discharge and decreasing the discharge capacity.

Example 8:

The five kinds of powder obtained in Example 7 were subjected to the X-ray powder diffraction, thereby obtaining crystallite sizes in accordance with the above-mentioned method. The obtained results are listed in Table 1. Among these powder, by using the powder having the molar ratios  $x$  of 0.02 and 0.005, plate batteries (in which a liquid electrolyte was LiPF<sub>6</sub>/EC+DMC+BMC) were manufactured to be subjected to an overcharging test as follows:

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The batteries were charged by a constant current and voltage under a condition of a maximum charging voltage of 4.3 V, a charging current of 0.3 mA/cm<sup>2</sup> and a charging time of 40 hours, and then were discharged by a constant current under a condition of a minimum discharging voltage of 3.0 V and a discharging current of 0.03 mA/cm<sup>2</sup>. The charging voltage in this example was 4.3 V, which is a severer condition than in Comparative Example 5, where the charging voltage was 4.2 V.

The charge capacity and the discharge capacity of the battery using the powder with the molar ratio  $x$  of 0.02 were 246 mAh/g and 191 mAh/g, respectively. The charge capacity and the discharge capacity of the battery using the powder with the molar ratio  $x$  of 0.005 were 247 mAh/g and 207 mAh/g, respectively.

When the charge/discharge was repeated under the same condition, the charge capacity and the discharge capacity of the battery using the powder with the molar ratio  $x$  of 0.02 became 191 mAh/g and 191 mAh/g, respectively. The charge capacity and the discharge capacity of the battery using the powder with the molar ratio  $x$  of 0.005 became 206 mAh/g and 206 mAh/g, respectively.

Thus, it was found that the battery using the powder

with a crystallite size of 700 angstrom or less was not excessively charged even when supplied with a high voltage of 4.3 V for a long time, which is not the case with the battery of Comparative Example 5. Further, it was found that the efficiency of the charge/discharge of such a battery was not degraded, and that the discharge capacity was substantially maintained. In this manner, an excellent overcharge resistance can be attained by using powder with a crystallite size of 700 angstrom or less.

Example 9:

In Example 7, the initial charge capacities of the batteries using the powder with the molar ratio  $x$  of 0.05, 0.02, 0.01, 0.005 and 0.001 were 217 mAh/g, 218 mAh/g, 237 mAh/g, 235 mAh/g and 238 mAh/g, respectively. The rise of the discharge capacity was quicker in the battery with the initial charge capacity of 220 mAh/g or more. Therefore, the relationship between the charge capacity and the quickness of the rise of the discharge capacity was studied by using the battery using the powder with the molar ratio  $x$  of 0.02.

By using the powder with the molar ratio  $x$  of 0.02 obtained in Example 7, two plate batteries (in which a liquid electrolyte was  $\text{LiPF}_6/\text{EC}+\text{DMC}+\text{EMC}$ ) were manufactured. The cycle characteristics of the batteries were determined under

the same condition as in Example 7 except that the initial charging time was respectively set to be 15 hours and 24 hours, which was 8 hours in Example 7.

The variation of the discharge capacity up to the 15th cycle is shown in Figure 7. In this graph, the capacity is normalized for comparison by using the capacity in the 15th cycle as 1. When the discharge capacity was 220 mAh/g or more, the increasing behavior of the discharge capacity was found to be improved. Specifically, it was found that the discharge capacity was risen by approximately the 5th cycle.

Thus, when the charge capacity at the time of the production of a battery is set to be 220 mAh/g or more per weight of lithiated nickel dioxide containing gallium, the initial overvoltage can be decreased and the rise of the discharge capacity can be quickened.

Although the battery was charged at 220 mAh/g or more merely once in the 1st cycle in this example, the battery can be charged in the 2nd or later cycle and twice or a larger number of times.

As described above, the present lithium secondary battery has an excellent cycle characteristic and overcharge resistance even when charged/discharged at a high capacity, and can attain a high energy density because it exhibits a

high discharging voltage. Accordingly, the present lithium secondary battery is extremely valuable in the field of industry.

Example 10:

An electrode and a plate battery for a charging/discharging test were manufactured as follows:

To a mixture of the powder obtained in Example 1 as an active material and artificial flaky graphite (KS15 manufactured by Ronza Co., Ltd.) as a conductive substance was added an NMP solution including PVDF as a binder so as to attain a composition ratio among the active material, the conductive substance and the binder of 87:10:3 (weight ratio). The resultant solution was kneaded to obtain a paste.

The paste was coated on one surface of an aluminum foil of 20  $\mu\text{m}$  thick and vacuum-dried at 150 °C for 8 hours and pressed to obtain a sheet. Then, the sheet was cut to obtain a cathode of 1.3 cm x 1.8 cm size.

Natural graphite (occurrence: Madagascar) powder which was heat-treated at 3000 °C, and having a number-average particle size of 10  $\mu\text{m}$ , a specific surface area of 9  $\text{m}^2/\text{g}$  according to a nitrogen adsorption method, a true specific gravity of 2.26, an interlayer spacing  $d_{002}$  of 3.36 Å in X-ray diffraction, and an ash content of 0.05% by weight, was mixed

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with graphitic carbon black (TB3800 manufactured by Tokai Carbon Co., Ltd.) subjected to graphitization at 2800°C so as to attain a composition ratio among the natural graphite powder and the carbon black powder of 95:5 (weight ratio).

One part by weight of a silane coupling agent (A186 manufactured by Nippon Unicar Co., Ltd.) was added to a mixture. After sufficiently mixing them, the mixture was vacuum-dried at 150°C to obtain mixed graphite powder treated with the silane coupling agent.

Then, to the mixed graphite powder treated with the silane coupling agent was added an NMP solution including PVDF as a binder so as to attain a composition ratio of the mixed graphite powder treated with the silane coupling agent and the binder of 97:3 (weight ratio). The resultant solution was kneaded to obtain a paste. The paste was coated on one surface of copper foil of 10  $\mu$ m thick and vacuum-dried at 150°C for 8 hours and pressed to obtain a sheet. Then, the sheet was cut to obtain an anode of 1.5 cm x 2 cm size.

By using the thus obtained cathode and anode, a plate battery was manufactured together with a liquid electrolyte (1M LiPF<sub>6</sub>/EC+DMC+EMC) and a polypropylene microporous membrane as a separator.

The plate battery obtained above was subjected to a

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charging/discharging test using using by a constant current and voltage and discharge by a constant current under the following condition:

Maximum charging voltage: 4.2 V

Charging time: 1 hour

Charging current: 7.7 mA

Minimum discharging voltage: 2.75 V

Discharging current: 7.7 mA

The potential of the cathode of the present battery went above 4.2 V (vs. Li/Li' ) at the last stage of charging under the experimental condition owing to the mixed graphite powder treated with the silane coupling agent as an anode active material.

The discharge capacity of 1st, 10th, 11th and 20th cycle were 3.67, 3.79, 3.86 and 3.76 mAh. The capacity holding ratios R1 and R2 were 1.032 and 0.967, respectively, and thus the battery exhibited an excellent cycle characteristic.

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What is claimed is:

1. A lithium secondary battery comprising:

a cathode including, as an active material, a material that can be doped/undoped with lithium ions;

an anode including, as an active material, a lithium metal, a lithium alloy or a material that can be doped/undoped with lithium ions; and

a liquid or solid electrolyte,

wherein said active material in said cathode is lithiated nickel dioxide containing gallium.

2. A lithium secondary battery according to claim 1,

wherein said lithiated nickel dioxide containing gallium satisfies the following relationship:

$$0 < x \leq 0.2$$

wherein  $x$  is a molar ratio of the gallium to a total amount of the gallium and nickel contained in said lithiated nickel dioxide.

3. A lithium secondary battery according to claim 1,

wherein said lithiated nickel dioxide containing gallium satisfies the following relationship:

$$0 < x \leq 0.05$$

wherein  $x$  is a molar ratio of the gallium to a total amount of the gallium and nickel contained in said lithiated



nickel dioxide.

4. A lithium secondary battery according to claim 1,

wherein said lithiated nickel dioxide containing gallium satisfies the following relationship:

$$0.001 < x \leq 0.02$$

wherein  $x$  is a molar ratio of the gallium to a total amount of the gallium and nickel contained in said lithiated nickel dioxide.

5. A lithium secondary battery according to claim 1,

wherein said lithiated nickel dioxide containing gallium is obtained by firing a mixture of a lithium compound, a nickel compound, and gallium or a gallium compound.

6. A lithium secondary battery according to claim 1,

wherein said lithiated nickel dioxide containing gallium is obtained by dispersing a nickel compound in an aqueous solution including a gallium compound and a water-soluble lithium salt, evaporating a water content of the resultant solution to obtain a mixture, and firing the mixture in an atmosphere containing oxygen.

7. A lithium secondary battery according to claim 6,

wherein said gallium compound is gallium nitrate, said water-soluble lithium salt is lithium nitrate and said nickel compound is basic nickel carbonate.

8. A lithium secondary battery according to claim 1,

wherein said lithiated nickel dioxide containing gallium is obtained by adding a basic compound to an aqueous solution of gallium nitrate to attain pH of 10 or more, dissolving lithium nitrate in the resultant solution, adding basic nickel carbonate thereto, then evaporating a water content of the solution to obtain a mixture, and fixing the mixture in an atmosphere containing oxygen.

9. A lithium secondary battery according to claim 8,

wherein said basic compound is lithium hydroxide.

10. A lithium secondary battery according to claim 1,

wherein said lithiated nickel dioxide containing gallium has a crystallite size of 700 angstrom or less determined through X-ray powder diffraction.

11. A lithium secondary battery according to claim 1,

wherein said lithium secondary battery is charged at least once at 220 mAh/g or more per weight, at the time of the production thereof, of said lithiated nickel dioxide containing gallium.

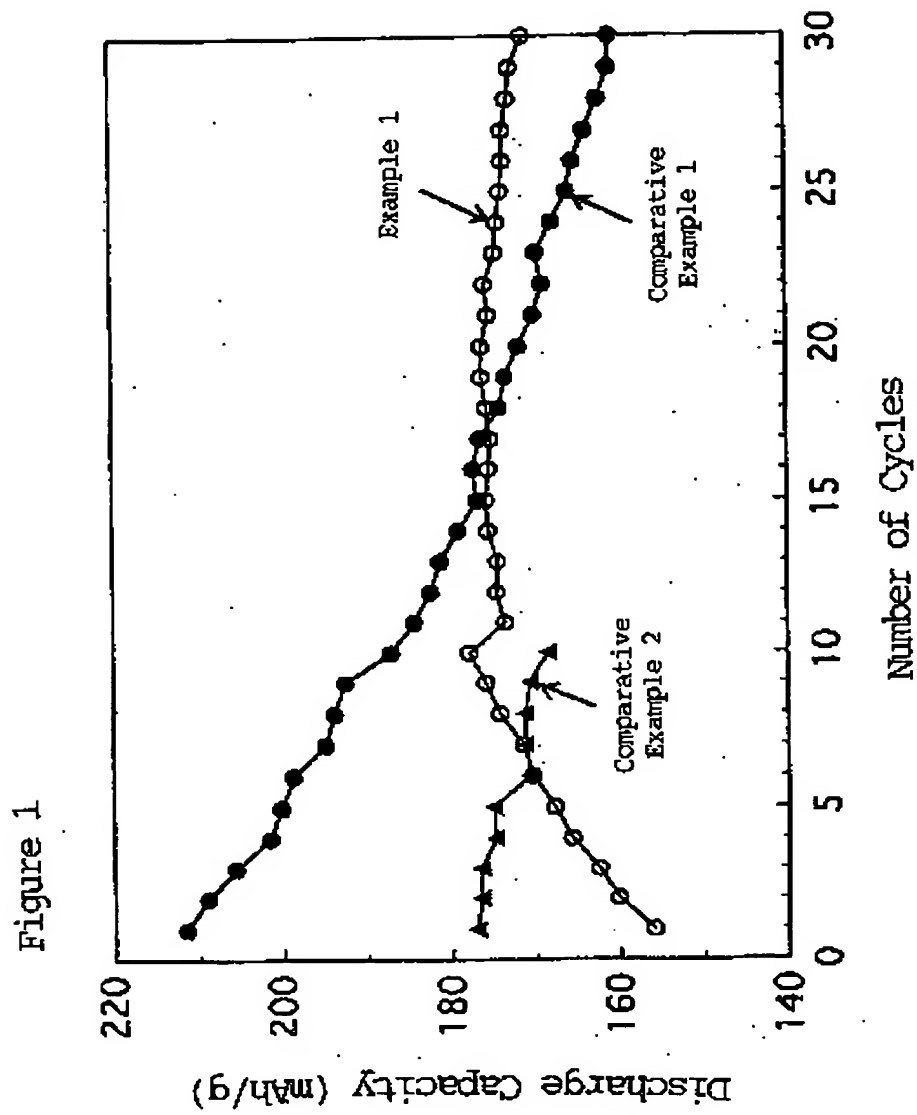
12. A lithium secondary battery according to claim 1,

wherein said anode includes graphite as a sole component or a main component of an active material, and said liquid electrolyte comprises ethylene carbonate, dimethyl carbonate and

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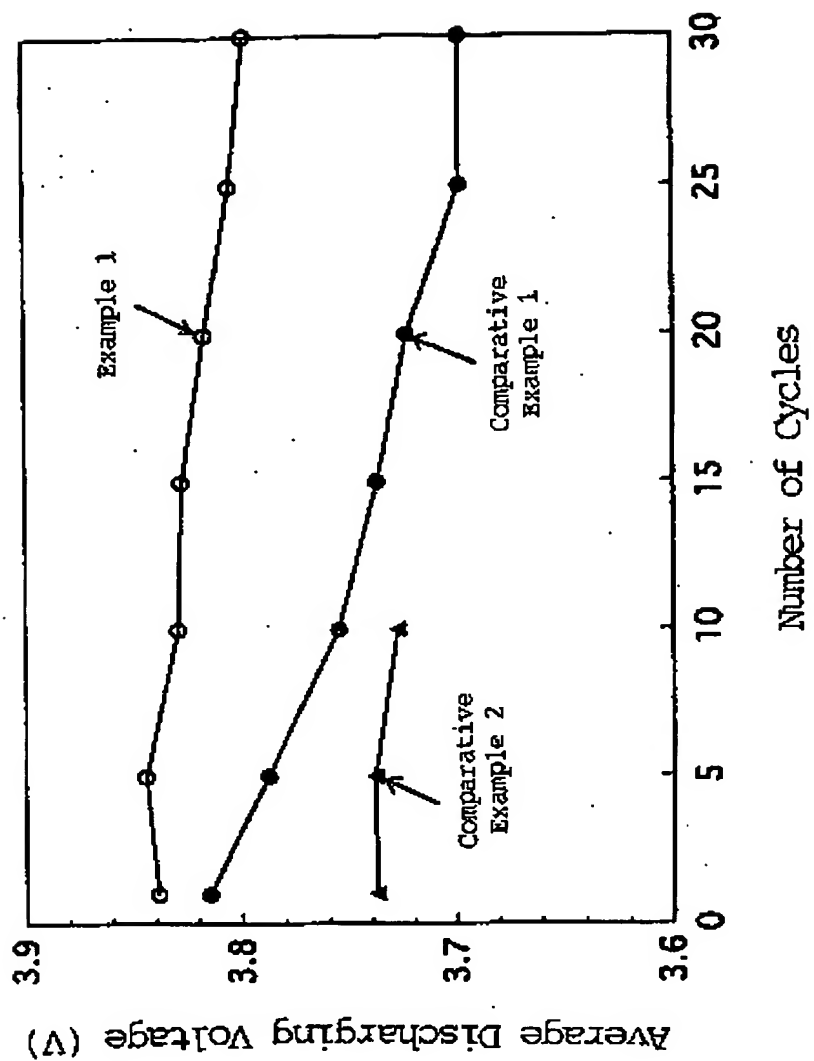
ethyl methyl carbonate.

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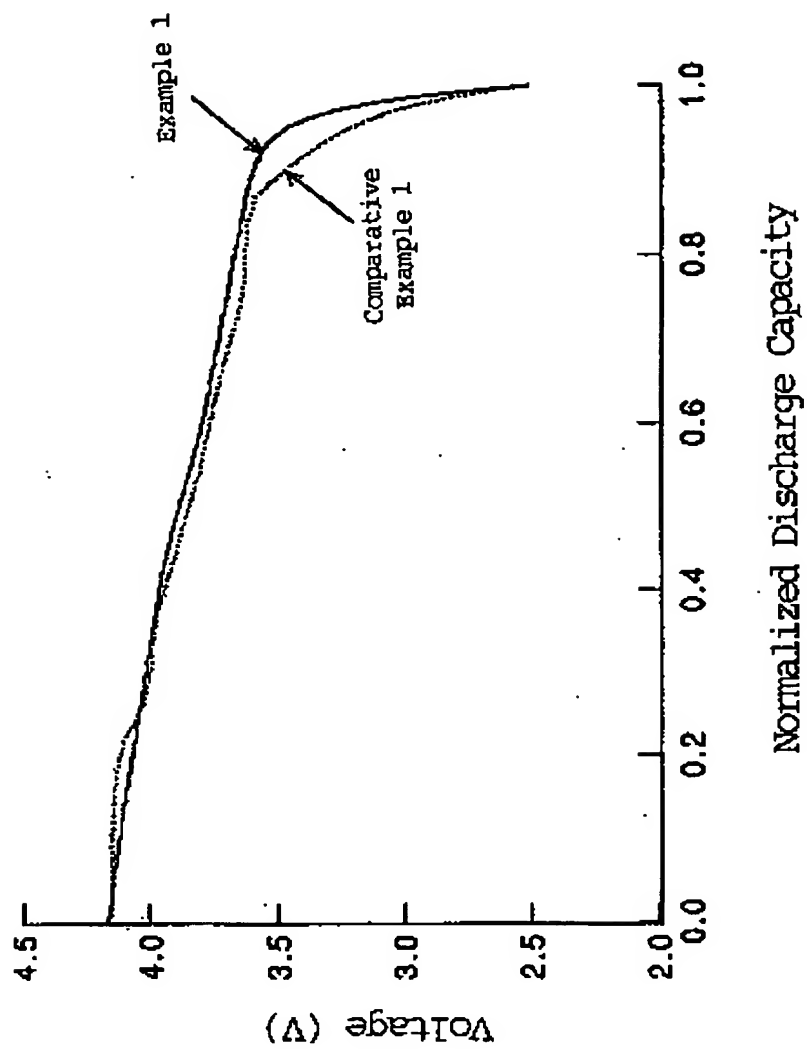
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Figure 2

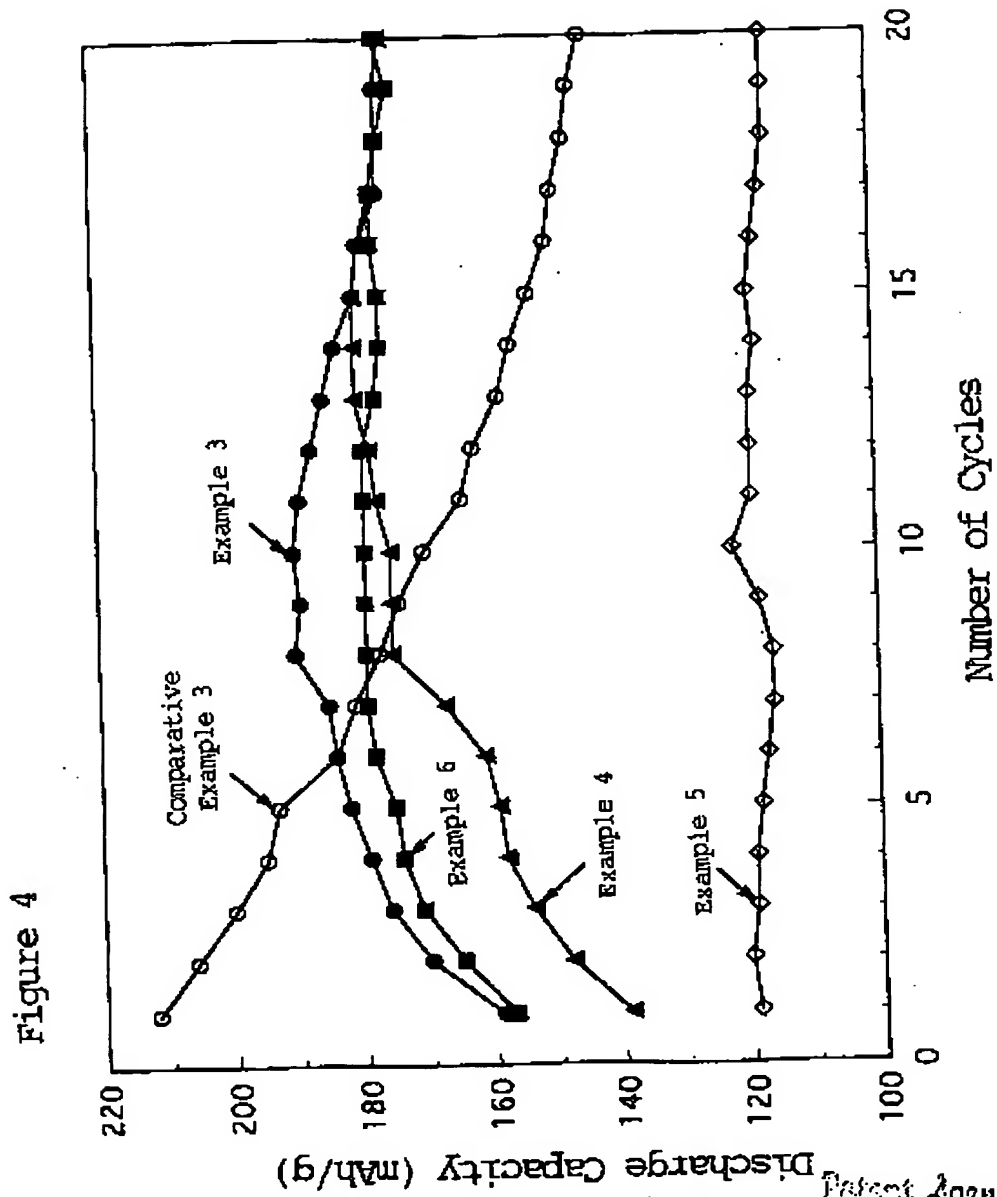


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Figure 3

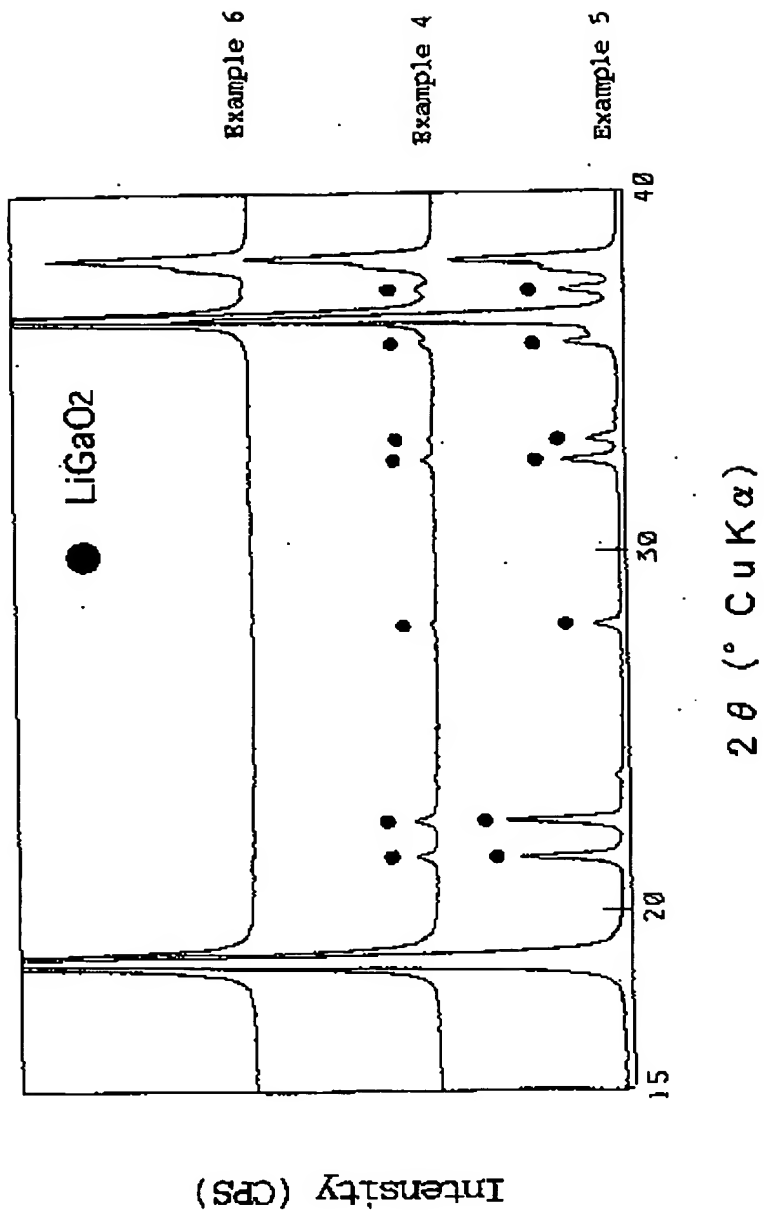


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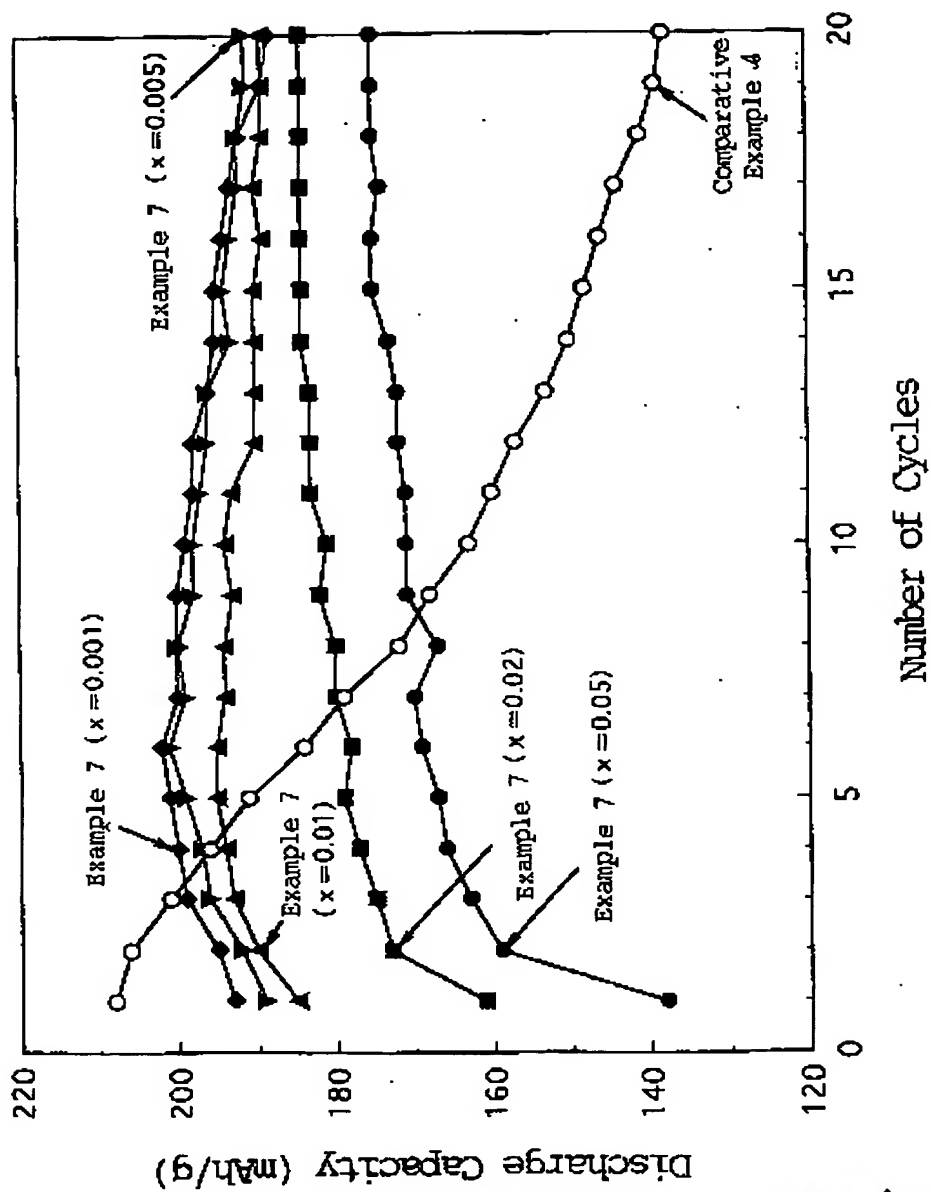
Figure 5



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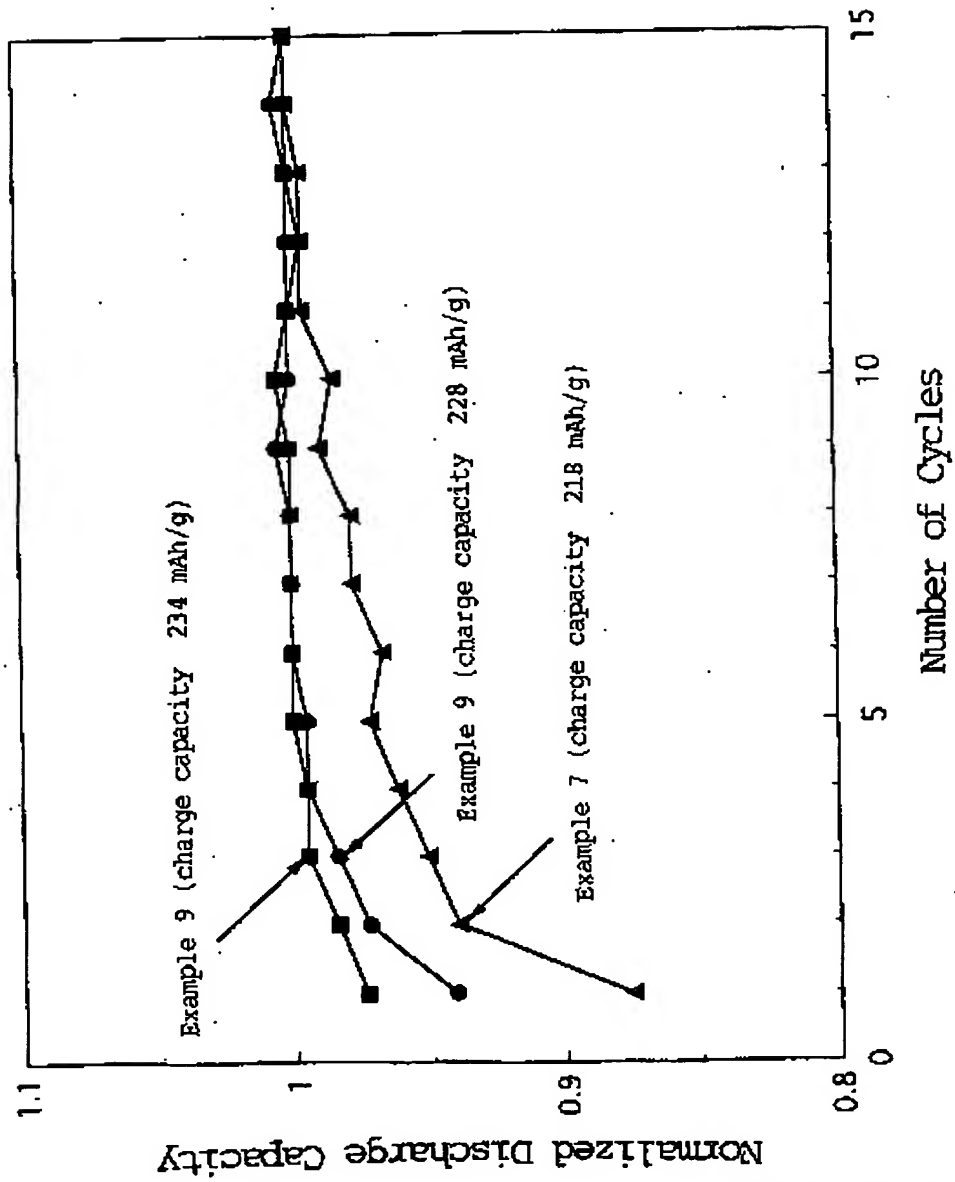


Figure 6



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Figure 7



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